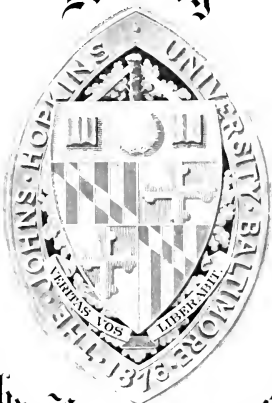


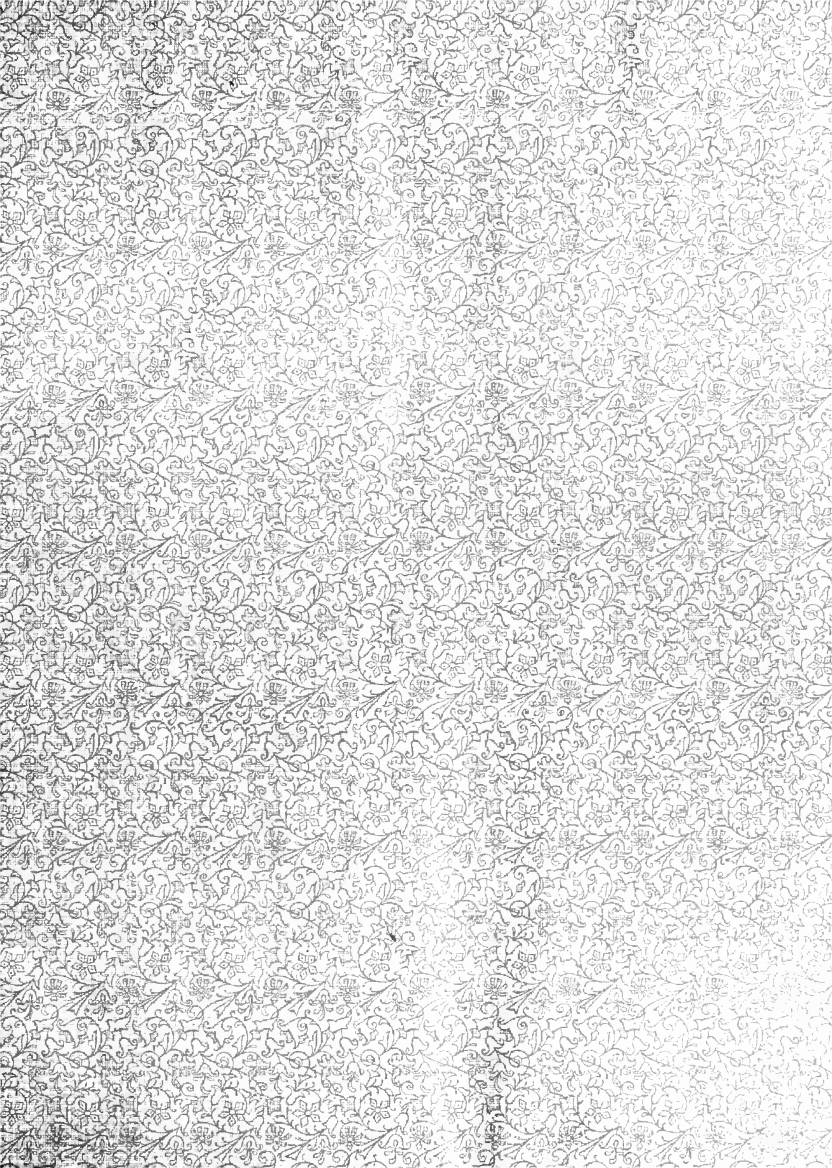
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An Investigation of Selenide and of its Reaction-products
with Phosphorus and with Phosphorous Pentachloride.

Dissertation

Submitted to the Board of University Studies of the Johns
Hopkins University in conformity with the requirements for the Degree of Doctor
of Philosophy.

- By -

William Phillips Winter.

1904

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Acknowledgment is gratefully made by the writer to the valued instruction which he has received in lecture-room and laboratory from Professors Rensen, Morse, and Jones.

This investigation was suggested by Professor Renouf and carried out under his guidance. To him the writer desires to express gratitude for his cooperation and helpful counsel.

The advice of Professor Morse has been frequently sought and it has proved most helpful. From Dr. Wilson and Professor R.W. Wood assistance has likewise been received which is hereby acknowledged.

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Historical. -

Sodium amide was first prepared nearly a century ago. Gay Lussac and Thenard ¹ and, independently, Sir Humphrey Davy ² while carrying on experiments to determine the composition of ammonia discovered at about the same time the amide of sodium and of potassium. They led a strong current of dry ammonia over sodium heated at 500° to 400° for several hours. Hydrogen was evolved and a more or less crystalline mass remained.

For many years sodamide was described in chemical literature as a dark olive-green substance, and at the same time it was stated that the glass of the retort was rapidly attacked.

In 1894, Titherly ³ made a careful study of sodamide and came to the conclusion that impurities in the sodium used by earlier experimenters as well as the constituents of the glass of the vessels in which it was made were responsible for the dark color of the product. He found that neither porcelain nor platinum long withstood the corrosive action of the compound. Retorts of iron or silver were not affected and in such vessels he stated that 500 grams or more of sodamide could be safely made at one time, whereas the earlier experimenters could prepare no more than from 2 to 10 grams at one time in retorts of glass.

In the present investigation it was found that a silver plated crucible was attacked to such an extent that the silver coating was entirely removed in the course of one experiment. Iron, if free from carbon, is very slowly acted upon.

Properties. -

Sodamide can be kept for a considerable time in dry, air-tight jars. Moisture rapidly decomposes it into ammonia and sodium hydroxide. If thrown into water, the rapid decomposition and evolution of gas

1. Recherches Physico-chimiques 1, 357-358.

2. Phil. Trans. (1809) 1, 39.

3. J. Chem. Soc. London 65, 504.

produces so much heat that the particles assume the spheroidal form and swim about on the surface of the water in much the same manner as does sodium until solution is complete. Usually the globule explodes with a sharp detonation characteristic of unstable nitrogen compounds and it was this that first suggested the possibility of the presence of a triazotate or similar compound as a working hypothesis.

The globule on explosion breaks into small particles which may be projected to a considerable distance. This explosion has been noted to occur more frequently when the water has become heated. The globules undergo peculiar physical changes. They change from white, to yellow, to brown, and sometimes to black; and the violence of the final explosion seems to increase with increasing depth of color. Sodamide which, through long keeping, has become yellow in color seems to be more susceptible to these color changes and to decompose more violently than that freshly made.

Sodamide is rapidly decomposed by absolute alcohol with evolution of ammonia and formation of sodium ethylate. The alcohol is heated to boiling if the sodamide be added rapidly but, since it does not float upon the alcohol, there is no final explosion.

Sodamide, which has undergone the color change referred to above, imparts this color to the alcohol and the latter becomes colored dark brown. The depth of tint which the alcohol assumes is out of all proportion to the amount of color in the sodamide used. Perfectly fresh sodamide imparts no appreciable color to alcohol. The color is not due to an iron salt, for, although the sodamide was made in a wrought-iron retort, it did not give the prussian blue reaction for iron when dissolved in water and treated with hydrochloric acid and ferrocyanide of potassium, and it yielded only a slight tinge with sulphocyanide of ammonium. Analysis of earlier workers. —

— Gay Lussac and Thénard¹ and also, Davy¹ attempted to analyze sodamide. The latter plunged pieces of it under the mouths of jars filled with water and he found that in addition to ammonia a

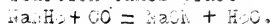
1. Loc.Cit.

"nonabsorbable" gas was given off which, by explosion in a eudiometer, was found to be hydrogen.

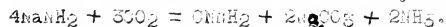
Gay Lussac and Thénard, by strongly heating the substance, obtained from it 2 / 5 of the ammonia that had disappeared in the reaction. At a stronger heat hydrogen and nitrogen gases were formed in the ratio of 2.5 of the former to one of the latter in quantities to account for 1 / 5 more of the ammonia, and decomposition of the residue by water or acids yielded the remaining 2 / 5. In addition to the fact that their hydrogen-nitrogen ratio is less than the theoretical for ammonia, it is also to be observed that all of the nitrogen thus obtained is, so far as their report of the analysis indicates, derived from the decomposition of ammonia.

Beilstein and Geuthner¹, in 1858, used the same method of formation for sodamide and gave the same description of the product as the discoverers. The method of analysis used by them consisted in determining the ratio of sodium to nitrogen by decomposition of the sodamide with strong hydrochloric acid, sodium and ammonium chlorides being formed in the reaction. They also investigated the reactions of sodamide with the oxides and the bisulphide of carbon.

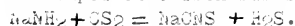
When sodamide is heated in a stream of carbon monoxide the following reaction takes place:-



In the same manner carbon dioxide yields:-



The vapor of carbon bisulphide yields:-



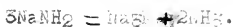
This, and the work of Wislicenus quoted farther on, seems to be the only work done with sodamide as a reagent in the field of inorganic chemistry. #

1. Ann. Chem. Pharm. Liebig 108, 88.

After the completion of the present work and while the manuscript was being written, the writer was permitted, through the courtesy of the editor of the Journal of the American Chemical Society, to read the manuscript of the forthcoming article by Dennis and Brown on the preparation of sodamide and of sodium triazolate by a modification of the method of Wislicenus. Their method for preparing sodamide is evidently an improvement in certain features over any hitherto used.

4.
 Titnerly's recent careful work, already mentioned, confirmed the analytical results of the earlier workers. He employed two different synthetical methods of analysis. The first was to convert a known weight of sodium into sodamide, determine the increase in weight and from that estimate the amount of sodium in the compound. The second method was to determine the ratio of the hydrogen given off to the residue of ammonia which disappeared in the formation of the compound. It was evident that $\text{NH}_2:\text{H}=16:1$; of $\text{NH}:\text{H}_2=15:2$, and of $\text{N}:\text{H}_3=14:5$. The mean of three determinations gave $\text{NH}_2:\text{H}=15.99:1$. The results of both analyses, therefore, pointed conclusively to the accepted formula, NaNH_2 , for sodamide. Titnerly then investigated the possibility of the formation of disodimide and of sodium nitride by the substitution of a second and a third hydrogen atom, respectively, of ammonia by sodium. After careful experiments, the details of which can not well be described here, he concludes that but one ammonia hydrogen atom could be thus directly substituted, although he later showed that certain radicals could be introduced into the place of one or both the remaining hydrogen atoms ¹. According to Dennis ² disodimide is formed by insufficient heating of sodium in ammonia.

The discoverers of sodamide had stated that if sodamide be strongly heated it decomposes in accordance with the equation:-



until quite recently this method for the formation of the nitride of sodium has been widely published. Titnerly was unable to obtain a trace of sodium nitride from his pure sodamide but he showed instead that strong heat breaks down the compound into its elements. He concluded therefore that the black powder described as nitride by Davy and others consisted of impurities undoubtedly present in the sodamine used.

1. J. Chem. Soc. London 71, 460.

2. Loc. Cit.

Preparation of sodamide.

Figure 1 represents the apparatus devised in this laboratory for the preparation of considerable quantities of sodamide at one time.

It is simple in construction and can be put together from apparatus available in almost any laboratory.

(A) is a flask in which concentrated ammonia water is heated with a low flame. (B) is an empty gas-washing bottle, kept cool to condense excess of moisture. 1, 2, 3, and 4 are drying towers filled with soda-lime. (C) is a tube filled with pieces of sodium. It may conveniently be about 40 centimeters long. (D) is a wrought-iron retort made in two parts which fit together at the flange in the center. It is capable of holding about 200 grams of sodium when filled nearly to the flange.

Before heating the sodium in the retort, ammonia is passed for a considerable time through the apparatus to drive out the air, and at the conclusion of the experiment the formed sodamide is allowed to cool in a current of the same gas. It is well to have a second flask containing ammonia water at hand to attach to the apparatus whenever the evolution of ammonia from the first one becomes slack, since it is important to have a continuous supply of ammonia.

The time of heating was purposely varied in order to determine whether this had anything to do with the gases yielded in the decomposition of sodamide by water.

The mysterious presence of free nitrogen among the products of the decomposition of one of the compounds to be described in this paper led to a somewhat extended investigation of sodamide itself. Sodamide had entered into the reaction and was the only nitrogenous component employed. The decomposition of the substance was made under conditions which precluded the possibility of the dissociation of ammonia into its elements. The method of analysis was a volumetric gas determination and the apparatus in which it was carried on will be briefly described here since it was devised and used in a long series of experiments.

6.

The apparatus (see Fig's. 2 and 3) was first filled with carbon dioxide dried by sulphuric acid, the gas (Fig.8) entering at (D) and escaping at (E). The weighed substance was introduced into (A) and the current of carbon dioxide continued until the gas issuing from (E) was completely absorbed by a strong solution of caustic soda. Without removal of the stoppers the tubes were shifted into the position shown in figure 2, the stopcock of (B) closed and the funnel filled with recently boiled distilled water. The tube(D) was quickly connected to the capillary of a Hempel's burette(F) completely filled with a 10% solution of caustic soda. Water was slowly dropped upon the substance in (A), diminished pressure being produced by lowering the communicating arm of the burette. When the reaction was over, water was allowed to completely fill the whole apparatus to drive over the last portions of gas. The burette was then disconnected, well shaken to absorb all carbon dioxide and ammonia, and the remaining gases were absorbed, where possible, in gas pipettes or determined by means of eudiometric methods.

In certain cases where it was desirable to establish without question the identity of nitrogen among the gases, known volumes of it, deprived of the presence of other gases, were transferred under precautions which precluded contamination with air to a short eudiometer specially adapted for use with high voltage currents. Excess of oxygen was added and the mixture was sparked in the presence of a little caustic potash for several hours. The remaining gas was then completely absorbed by thosorus.

In the analyses given, sodamide I was made by heating 175 grams of sodium for four hours with the full flame of a bunsen burner. At the end of the operation the crystallized sodamide which in all cases was of a white color, was broken away from some unchanged sodium. Sodamide II was made from 60 grams of sodium heated 3 and 1/2 hours. There was no apparent excess of sodium. Sodamide III was made from 110 grams of sodium heated strongly for 3 hours- no excess of sodium. Sodamide IV was made from 42 grams of sodium heated 1 and 1/4 hours. The excess of sodium was separated from the sodamide as described above.

Socamine was made by heating 50 grams of sodium 4 hours. There was no excess of sodium. All the samples were at once transferred to well-stoppered glass bottles and kept in the dark.

For the analysis small portions were taken from different parts of the material, finely ground, and placed in glass-stoppered weighing tubes in calcium chloride desiccators. The decomposition was effected by water in the apparatus described. The latter had been previously tested by allowing it to stand for 14 hours under the diminished pressure produced by the difference in level of the two communicating arms of the Hempel's burette amounting to about 4 feet. No change of level was noted, thus indicating that there was no entrance of air by leakage into the apparatus during the experiment.

The reaction with the first drop or two of water is extremely violent. 60 to 80 cubic centimeters of gases are formed and driven over into the burette within the first few seconds, and the generator becomes very hot. Since most of the gases are ammonia and carbon dioxide the absorption is so rapid that, notwithstanding the diminished pressure, the liquid is sometimes drawn back into the generator with resultant explosion of the latter from confined gases. The partial combination that takes place between some of the ammonia and the carbon dioxide is also responsible for the rapid back-suction. In practice it was found necessary to introduce a measured quantity of pure oxygen into the Hempel's burette to act as a sort of cushion to regulate the absorption.

Table of Volumetric Gas Determinations of Different Samples of Sodamides.

Sodamide I

Wt. in gms.	Total c.c. of gases	% of N ₂	Remarks.
0.5957	17.25	16.09	
1.4145	37.65	19.25	
0.2557	9.80	32.37	
0.8410	22.9	33.95	
.7070	18.3	33.42	
0.6965	17.	41.55	
0.8464	21.4	44.45	
0.6589	20.9	53.53	
0.4772	13.8	53.62	after standing 5 weeks
0.4375	15.7	55.81	

Sodamide II

1.1229	4.4	--	} trace of hydrogen on explosion.
1.3469	5.6	--	
1.1349	4.3	35.05	

Sodamide III

0.8513	5.	72.53	
0.9819	3.34	75.64	
0.7777	4.3	85.13	
0.6957	4.3	89.14	after standing 12 weeks
0.9195	3.65	92.	after standing 14 weeks

Sodamide IV

0.6250	13.75	6.15	} freshly analyzed
0.7525	28.	5.22	

Sodamide V

0.6221	1.2	49.16	} freshly analyzed
0.6654	1.2	51.66	
0.4122	1.8		after 5 weeks; no color change; trace of hydrogen.

portion kept 5 weeks with resultant change of color excluded on analysis.

Sodamide III was not analyzed until some weeks after its preparation. Frequent explosions of the generator, and other difficulties in the application of the method with the apparatus at hand hampered to some extent the work. However it was not sought to set forth by this method an exact analysis of sodamide for the apparatus with which to do the work was that which would asertain to a "proximate" and not to an "exact" series of gas determinations. Quite exact quantitative analyses have been repeatedly made by better methods.

As has been stated, the purpose was to seek, if possible, the explanation for the presence of this free nitrogen among the decomposition products of sodamide, and to the facts deduced from the analyses bearing on this phase of the problem we now turn.

- 1.- Sodamide is not a stable substance; it changes its composition not only from frequent opening but apparently under certain conditions on long standing in closed vessels.
- 2.- it is only apparently homogeneous; sodium hydroxide and free sodium in minute particles being two adulterants always present, and evidence seems to be conclusive that a number of sodium compounds, to which reference will be presently made, are to be found in traces in it.
3. Sodamides I and IV were made to contain excess of sodium. The free metal could be separated quite readily since the sodamide is white, brittle and crystalline while the sodium is dark, waxy, massive, and floats upon the top of the sodamide which has been formed. Nevertheless the analyses of these, when contrasted with the other samples, show a relatively large gas evolution and (naturally) a low nitrogen percentage because of the hydrogen present. The only other gas found in the products of decomposition of sodamide by water, besides ammonia, was hydrogen and the percentage of this gas can therefore be simply deduced from the percentages of nitrogen. The explanation for the liberation of this hydrogen is that minute particles of sodium become encrusted with sodamide in the retort and escape the action of the excess of ammonia. Accordingly the proper preparation of sodamide requires a prolonged heating in a slow current of ammonia.

4. When sodamide is thus made, the total gas insoluble in water and in sodium hydroxide solution falls to a minimum but is never zero, and at the same time the percentage of nitrogen rises nearly to 100%.

5. Another striking fact to be observed in the analyses is that invariably the percentage of nitrogen rose rapidly when the compound is kept for some time.. Reference to this will be made again later.

6.- There is an actual diminution in the amount of hydrogen found among the decomposition products of sodamide that has stood for some time, and in many cases an actual and not merely a relative increase in the amount of nitrogen. The former is to be accounted for as follows. The minute particles of sodium are slowly acted upon at the ordinary temperature by the atmosphere of ammonia always to be found over sodamide, and thereby new sodamide is formed.

But while the hydrogen evolved thus falls to a minimum the total amount of gas formed does not fall in like proportion. On the contrary it more often increases. This points to a subtle change going on simultaneously with the disappearance of the sodium whereby a compound capable of yielding nitrogen is being continually formed. This hypothetical compound is never absent in any sodamide we have made or examined. An average of three determinations of gases insoluble in water yielded by a freshly prepared sodamide made to contain a minimum of free sodium gave 4.5 cubic centimeters of gases per gram of sodamide. The same sample four weeks later gave as an average of three determinations 5.9 cubic centimeters of gases per gram and the volumetric percentage of nitrogen was increased while that of hydrogen had decreased. This relation is also well illustrated in the results given in the table (pages 8).

It has been already mentioned that Beilstein and Geuther ¹ had noted the formation of cyanamide, CNNH_2 , when sodamide is heated with dry carbon dioxide. Since the latter gas was used to displace air in the apparatus in which the sodamide was decomposed, and since the considerable heat of the reaction might have formed small quantities

1. Loc. Cit.

of cyanamide whose subsequent decomposition might account, in some unexplained way, for the presence of nitrogen, it was thought best to repeat the experiments with some other gas to see whether any change would occur in the amount or the character of the gases developed. Oxygen suggested itself as a gas which could easily be absorbed by alkaline pyrogallol solution, but attempts to use it resulted in explosions of the mixture of hydrogen and oxygen which was detonated by the minute flame produced when the first drop or two of water strikes sodamide containing the usual trace of free sodium. Nitrogen was then used and to determine the increase of gas the apparatus was calibrated in terms of the graduation of the Hempel's burette. 0.5901 grams of sodamide yielded, when decomposed by water in the ~~presence~~ presence of nitrogen, 43.25 cubic centimeters of gases. Deducting 41.45 cubic centimeters for the capacity of the apparatus, there remains 4.8 cubic centimeters as the amount of gases attributable to the decomposition.

0.6937 grams of the same sodamide decomposed a few days previously in the presence of carbon dioxide yielded 4.6 cubic centimeters of gas. It was evident from this that carbon dioxide did not exert any appreciable influence on the amount of gas evolved by the decomposition of sodamide with water. Examination of the solution left in the generator showed only a trace of sodium cyanamide as a by-product of the reaction, and it is not at all clear how its presence in considerable amount could have affected the percentage of nitrogen.

In the second place it was assumed that if heat had anything to do with the evolution of nitrogen from sodamide in its decomposition, the amount could be diminished by working near the zero temperature. Accordingly the generator (A, Fig. 2) was immersed in ice-water and the funnel filled with the same.

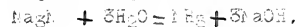
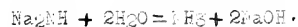
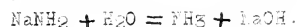
0.5747 grams decomposed under these conditions yielded 4.3 cubic centimeters of gases. This is quite comparable with the yield at ordinary temperatures. The conclusion is then unavoidable that neither temperature nor the

12. nature of the diluent gas exerts any appreciable effect on the amount of gas generated, and the presence of free nitrogen constantly among the products of decomposition of sodamide by water can only be ascribed to the presence of a compound of the triazotate order whose instability can account for the phenomena as observed.*

Three theories have been advanced to account for this nitrogen.

1.- That the considerable heat suddenly developed by dropping water on sodamide dissociates some ammonia into its elements. This is highly improbable for, if it were the case, the hydrogen formed should bear a simple ratio to the nitrogen, or at any event should be in excess. Inspection of the analyses show that in many cases only traces of hydrogen are present.

2.- That minute quantities of disodimide or of sodium nitride break down yielding nitrogen. This is equally untenable for not only has their formation in this manner been shown to be highly improbable but, even if present, such compounds being ammonia derivatives would yield ammonia on treatment with water:-



3.- That traces of sodium or ammonium triazotate, Na_2Azo_3 or NH_4Azo_3 , would yield nitrogen on decomposition through the sudden heat developed by the addition of the first drop or two of water. There is no evidence that this class of salts decompose quietly though some of them explode on sudden heating¹. It was noted that the material in the generator, usually about 500 milligrams, was spattered about violently by the first contact with water and there is unquestionably a very sudden rise in the temperature of the mass.

* The invariable presence of nitrogen in the decomposition of sodamide by water is not to be referred to a constant error of some sort in the conduct of the experiment, for this same method was repeatedly used in the analysis of a substance made from sodamide which yielded on decomposition by water chiefly hydrogen and phosphine. In the greater number of instances no nitrogen could be detected in the gas evolved. To this work reference is more fully made in the latter part of this paper.

1. Ber. d. Chem. Ges. 24, 3346.

W. Wislicenus ¹ has described a simple and effective synthesis of sodium triazotate depending on the use of sodamide. It is essentially that if nitrous oxide be passed over sodamide heated to its melting point, 1550-1600°, the following reaction occurs with some energy:-



The presence of metallic sodium or of strong bases seems necessary and therefore the reaction cannot be made to take place between nitrous oxide and ammonia. The yield is about 50%, and the method is capable of general use as a source of triazotic acid.

Dennis and Brown ² have, within the present year, made a study of this method and suggested improvements which afford much more satisfactory yields.

If the presence of sodium triazotate is to be assumed in the sodamide we have used, the only way to account for its presence is as follows. It is well known that the oxidation of ammonia leads through a series of hypothetical compounds to the well-known nitrous and nitric acids,-



If there is insufficient oxygen to carry the oxidation farther, the process stops at this stage and the unstable hyponitrous acid may readily break down into nitrous oxide and water.

The presence of traces of oxygen is not unlikely in ammonia generated from strong aqueous solution and passed through large drying towers of soda-lime. Moreover the short exit tube of the retort in which the sodamide is made, and the central flange of the body of the retort permit slight access of air to the mass within.

Very little sodium triazotate is demanded to account for the nitrogen formed. Sodamide yielding 5.5 cubic centimeters of nitrogen per gram would require less than one percent of sodium triazotate.

To account for the increase of nitrogen obtained by decomposing sodamide which has been kept in stoppered bottles for some time, it must be

1. Ber.d.Chem.Ges. 25, 2084.

2. Loc.Cit.

further assumed that the oxygen of the air, the ammonia, and the traces of sodium can slowly react at ordinary temperatures in the way that has just been pointed out.

In the attempt to isolate this compound, experiments were undertaken which led into a qualitative study of the changes which sodamide undergoes on keeping. A number of interesting facts were ascertained and furthermore a line of investigation was indicated which it was impossible for the writer in the limited time at his disposal to fully exploit.* The phenomena which led to this part of the work are here recapitulated and, after a brief description of the work done, some theoretical conclusions are appended which await further confirmation.

1. The color change in sodamide on keeping.
2. The violence (often explosive) of the decomposition of sodamide by water.
3. The examination of the solution obtained through this decomposition.
4. The two-fold source of nitrogen in the breaking down of the colored variety of sodamide by water.
5. The reaction with alcohol.
6. The cyanamide reaction.

The color change is evidently the key to the explanation of some of the other phenomena. The facts are these:-

Sodamide, when freshly made, is white, solid, and crystalline. Upon long keeping it becomes, with few exceptions, yellowish-brown, somewhat porous, and it loses its crystalline appearance. That this was not due to change induced by atmospheric moisture and consequent breaking down into sodium hydroxide colored by iron was assured by analysis of one specimen of sodamide which had undergone the color change. It was shown that deterioration had only partially taken place for the ammonia found, calculated

* The work is not described in this paper in the order in which it was carried on. The reactions of sodamide with phosphorous pentachloride and with yellow phosphorus were first taken up, and as much of the time as was left was devoted to the study of sodamide itself.

as NH_2 gave 35.85% and 35.61% as the result of two determinations, whereas the theoretical amount is 41.07%. The negative result of the test for iron has been already given.

For a considerable time the change was ascribed to the action of light. But samples kept in dessicators both in the light and in the dark showed conflicting results.

It was shown, however, that the change is in some way dependent upon the amount of dry air which comes into contact with the sodamide, and upon the length of time of exposure to the air; for it was observed that:

1. The sodamide which had been kept longest had undergone the greatest change when conditions of treatment otherwise were the same.

Externally the lumps were covered with a white incrustation (probably of sodium hydroxide) but when broken open they were porous, friable, and colored throughout.

2. Powdered sodamide underwent this change of color much more rapidly.

3. Small bottles with accurately fitting stoppers, not opened repeatedly as most of the samples were, suffered little or no change in their contents.

The effect of this change upon the sodamide is very evident.

Two samples of the same material were powdered and so treated that air had more complete access to one than to the other. At the end of five weeks the one tightly closed had suffered no change in color, could be decomposed in the usual way in the apparatus shown in Fig. 2, and showed the usual diminution in hydrogen with but a slight increase in nitrogen.

The other portion was dark in color and exploded with violence, when the first drop of water was admitted under it from the funnel, in three successive repetitions of the experiment. When thrown into water it decomposed energetically with flame. Thrown into alcohol it left a considerable white residue. In all cases the decomposition of colored sodamide seems more violent than that of the white variety and, as already mentioned, the explosion of the globule which floats upon the surface of the water is more violent.

When the two varieties of sodamide are dissolved in alcohol, the yellow variety imparts a deep brown shade to the liquid and this is only partially discharged by acids. White sodamide imparts no color. An insoluble residue is left after the solution of the yellow variety. Decomposition of this by acids yields, as one of the products, carbon dioxide thus pointing to the existence of traces of sodium carbonate. It is in this residue that sodium triazoate should be found, if found at all, since sodium triazoate is almost insoluble in absolute alcohol.

The examination of the solution formed by throwing sodamide into water also gave distinctive reactions differentiating the yellow and the white varieties. Without exception the yellow sodamide solution responded to the various tests for nitrous acid, yielding fumes of nitrogen peroxide with excess of dilute sulphuric acid, and giving a deep brown coloration with meta phenylene diamine. The solution of the white variety failed to yield these tests.

In the theory already elucidated to explain the possible presence of a compound of the triazoate order, it is evidently only necessary to carry the oxidation of the ammonia one step farther to account for the presence of nitrous acid. The formation of nitrous acid after the sodamide has been kept for a considerable time and not during the process of its manufacture seems conclusive evidence that either the nitrogen of the air can enter into reaction with sodamide without the aid of heat, or, more probably, that the oxygen of the air can effect oxidation of the nascent ammonia formed by the slow breaking down of a part of the sodamide. This oxidation product would then combine with the base to form sodium nitrite. But since the latter is undoubtedly present, it is not at all unlikely that traces of sodium hyponitrite are also present for its formation would involve merely the supposition of the presence of one of the intermediate products of oxidation. And the presence of hyponitrous acid, as we have seen, renders possible, if not probable, the presence of sodium triazoate.

Hyponitrous acid, according to Hantzsch¹, exists in two stereoisomeric
 1.- Ann. Chem. Pharm. Liebigs 299, 67.
 Ber.d.Chem.Ges. 30, 2356.

varieties one of which, called isohyponitrous acid, yields no yellow precipitate with silver nitrate, but it gives a white precipitate with mercuric nitrate; the normal hyponitrous acid, on the contrary, yields yellow silver hyponitrite and no precipitate with mercuric nitrate. In applying this test there was obtained a slight precipitate with mercuric nitrate pointing to the existence of one of the above hyponitrous acids.

When the solution in water of the yellow sodamide was decomposed with dilute sulphuric acid in a small vessel from which the air had been displaced by carbon dioxide, a number of gases were evolved.

The apparatus was connected with a Hempel's burette in order to collect and examine the gases. Dilute sulphuric acid was admitted slowly through a dropping funnel and at first there was a considerable evolution of carbon dioxide. This, together with any ammonia which may have been disengaged before neutralization of the strongly alkaline liquid, was completely absorbed by shaking with the solution of sodium hydroxide in the burette. After the neutralization of the alkali, an excess of acid was introduced and the solution was boiled. The gases were completely driven into the burette and, after shaking, there remained a considerable residue unabsorbed.

By admitting this into a eudiometer partially filled with oxygen over water there was noted the formation of nitrogen peroxide and consequent diminution of volume through its absorption. But a residue still remained which did not combine with oxygen even on passing the spark.

Into another portion of the gas pure hydrogen was passed and the mixture was sparked, but there was no evidence of any combination having occurred. Hence it was highly improbable that either oxygen or nitrous oxide was present in any appreciable amount in the gases and the conclusion seemed unavoidable that the remaining gas was nitrogen.

A third portion was passed into a Bunsen gas pipette filled with aqueous solution of ferrous sulphate. The formation of the characteristic brown compound of nitric oxide with ferrous sulphate occurred and a residue of nitrogen remained. The nitric oxide was in slight excess as will be seen from the following results obtained by the

decomposition of three separate portions of sodamide, the lack of homogeneity in which has been shown elsewhere as well as in this series.

Table of Ratios of Nitrogen to Nitric Oxide.

1st portion-- in eudiometer with oxygen.

1.- 1 part nitrogen to 2.5 parts nitric oxide.

2.- 1 " " " 2.58 " " " .

2nd portion-- determined as above

1.- 1 part nitrogen to 1.5 parts nitric oxide.

2.- 1 " " " 1.4 " " " .

3rd portion. Nitric oxide absorbed by ferrous sulphate.

1.- 1 part nitrogen to 1.21 parts nitric oxide.

2.- 1 " " " 1.3 " " " .

While the decomposition of nitrous acid can account readily for the presence of nitric oxide and nitrogen peroxide, it fails completely to account for the presence of nitrogen.

Hyponitrous acid usually breaks down into nitrous oxide and water, but, when violently decomposed, water, nitrogen, and oxygen are produced. If both acids are present, secondary reactions between nitric oxide and oxygen would explain the absence of oxygen, and excess of nitric oxide would remain if nitrous acid were present in greater amount than hyponitrous acid as is, no doubt, the case.

The possibility that exists here for the formation and presence of other compounds in diminutive traces is evident from a consideration of such work as the following:-

VonBrackel¹ has obtained hydrazine from the reduction of hyponitrous acid. Hantzsch² has converted nitroso hydroxylamine into hyponitrous acid and has shown the possibility not only of stereoisomers of this acid but also of a structural isomer, nitramide, NO_2NH_2 .

Diters,³ van der Plaats,⁴ and Paal⁵ have each done work showing the intimate relationship that exists between nitrites, hyponitrites,

1. Ber. d. Chem. Ges. 33, 2115.

2. Loc. Cit.

3. Proc. Roy. Soc. XIX, 425.

4. Ber. d. Chem. Ges. 10, 1507.

5. Ibid 26, 1026.

hydroxylamine, hydrazine etc. and in many cases there are conflicting statements.

The study of the decomposition of sodamide by water has revealed some interesting facts concerning the nitrogen evolved:-

1. All sodamide, white or yellow yields nitrogen when decomposed by water in an atmosphere of carbon dioxide. This nitrogen is evolved in the presence of an excess of alkali.
2. Yellow sodamide in the above reaction when further treated with excess of acids yields a second portion of nitrogen and nitric oxide is also evolved.
3. White sodamide decomposed by water does not yield with excess of acids any gases which are not absorbed by the sodium hydroxide.

The significance of these facts is that a compound, at least analogous to a triazotate, is partially broken down in alkaline solution and completely decomposed by acids. A salt of nitrous or hyponitrous acids is indifferent to alkaline reagents but is decomposed by acids.

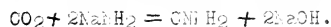
It will be necessary to prepare sodamide under the most varied possible conditions, to expose it to long contact with quantities of dry air both at ordinary and at somewhat elevated temperatures, and to verify by preparation in quantity of hyponitrous acids and its related compounds a series of reliable tests which may be employed in investigation of the yellow variety of sodamide. This work is not unimportant if sodamide is to be used as a reagent because of the complicated side reactions which such traces may render possible.

Sodium cyanamide.

In the course of this investigation it was noted that when a cylinder containing a small amount of water heated almost to boiling was filled with carbon dioxide in continuous supply and powdered sodamide was slowly sifted in from a specially arranged tube passing through the stopper, the particles of sodamide in falling through the carbon dioxide were heated to incandescence. Each addition of sodamide was accompanied by evolution of gas which was almost immediately dissolved as ammonium carbonate, and more carbon dioxide would then flow in. If the cylinder was tightly closed and the carbon dioxide supply shut

off, greatly diminished pressure resulted and the sodamide ceased to inflame. The latter also occurred when the temperature of the water fell much below 60° or if the carbon dioxide became diluted with nitrogen, hydrogen, ammonia or air. Pure oxygen added to the carbon dioxide seemed to increase the brilliancy of the combustion. There was no production of sparks whatever when sodamide was dropped into dry carbon dioxide. Qualitative examination of the solution within the cylinder at the close of the experiment showed that sodium cyanamide was present, and occurred most abundantly in those experiments that were rich in spark production. This method for the formation of cyanamide has not been hitherto described.

Beilstein and Ceuther¹ gave for the formation of cyanamide this equation



Drechsel² showed that this reaction was not an analogous one to the reaction, given by the same authors, to explain the action of carbon disulphide on sodamide, and that one or the other should be revised in accordance with what is commonly accepted as to the ability of sulphur to substitute oxygen in formation of homologous and analogous series. He accordingly stated that the reaction probably took place in three stages as follows:-

- 1.- $\text{CO}_2 + \text{NaNH}_2 = \text{OC}(\text{NH}_2)\text{Na}$ - sodium carbanate.
- 2.- $\text{H}_2\text{CO}_2\text{Na} + \text{heat} = \text{H}_2\text{O} + \text{NaCN}$ - sodium cyanate.
- 3.- $\text{NaCN} + \text{NaNH}_2 = \text{H}_2\text{O} + \text{NaNHCN}$ - disodium cyanamide.

That the disodium salt was formed, he showed by the fact that, whereas cyanamide breaks down at about 155° , and monosodium cyanamide, below a red heat, this substance was stable at much higher temperatures.

The quantitative analysis is best carried out with the silver salt, CnNaAg_2 , - a brilliant-yellow, amorphous precipitate produced by addition of ammoniacal silver nitrate solution to a solution of cyanamide or any of its salts. The precipitate was dried at 130° and analyzed as follows:-

1. Loc.Cit.
2. J.Prakt.Chem. (2), 11, 308; & 16, 203.

Quantitative analysis of sodamide.

No analyses of sodamide in the ordinary way involving the breaking down of the compound have been published; due, doubtless, to the difficulty of regulating the decomposition. Analyses to be of any value must also be made from freshly prepared material, for the composition varies from day to day and in different portions of the same mass. Owing to these facts synthetical methods of analysis are of more value.

However it was found that the substance could be decomposed within a pressure bottle in the presence of some acid which would dissolve the ammonia gas. The substance was weighed in a closed weighing bottle and after removing its stopper the bottle was placed in an upright position in a pressure flask containing a little hydrochloric acid. After 24 hours the bottle could be tilted to allow substance and acid to come into intimate contact.

The sodium was determined as sulphate after expulsion of the hydrochloric acid and the ammonia was distilled into a standard acid after liberation by means of excess of alkali hydroxide.

a. Determination of sodium.

0.2158 grams gave 0.3546 grams of sodium sulphate corresponding to 57.81% of sodium.

0.1662 grams gave 0.2934 grams of sodium sulphate corresponding to 57.25% of sodium. The theoretical amount required is 58.93%.

b. Determination of ammonia.

0.2515 grams gave 37.58% NH_3

0.5832 grams gave 37.91% NH_3 .

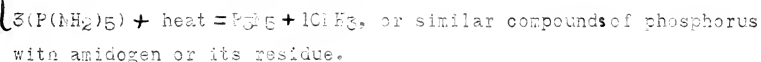
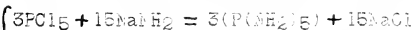
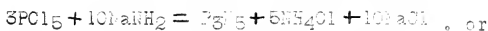
It has been stated that sodamide can be kept in a relative state of purity for a long time under dry benzene and in many syntheses the presence of the latter does not complicate the reaction.

Sodamide and Phosphorous Pentachloride.

The elements of which sodamide is composed, its constitution, its avidity for water and its behavior with many reagents lead one to the conclusion that it is an active and energetic reagent. Although it has not been used to any great extent in inorganic reactions, it has been used by Titherly ¹ in a series of organic syntheses in the course of which he pointed out that it is the hydrogen and not the sodium atom which is active. Freund and Speyer ² and others have also employed sodamide for organic work.

A number of weeks after the investigation herein described had been commenced Stock and Hoffman ³ published an account of the preparation of a new nitride of phosphorus, P_3NH_5 , by treating phosphorus pentasulphide with liquid ammonia and heating the complex compound formed. It may also be formed by heating the pentasulphide directly in a stream of ammonia gas to 230° .

It seemed not improbable that sodamide acting on phosphorous pentachloride could effect a transformation such as:-



The work of Joannis ⁴ who obtained boron triamide by passing the vapor of boron trichloride together with hydrogen through liquid ammonia; of Souff ⁵ who prepared a phosphoryl triamide, $PO(NH_2)_3$ from phosphorous oxychloride and dry ammonia; of Hugot ⁶ who worked with sod-ammonium, $NaNH_2$, on phosphorus and on arsenic; of Besson ⁷ who obtained

1. Chem. Soc. London 71, 490.

2. Ber. d. Chem. Ges. 35, 2321.

3. Ibid. 35, 514.

4. Compt. Rend. 135, 1106.

5. Ann. Chem. Pharm. 101, 299.

6. Compt. Rend. 121, 206; 126, 1719; 127, 553.

7. Ibid. 114, 1264.

as a final product phospham, PN_2H , from the double salt obtained by treating phosphorus pentachloride with ammonia; and of others who have used liquid ammonia or ammonia gas, points clearly to the fact that compounds containing ammonia-nitrogen have been made in considerable variety and are of unusual chemical interest.

Preparation.

When powdered sodamide and phosphorous pentachloride are brought together in small quantities in a dry test tube and the mixture slightly warmed a violent reaction ensues accompanied by flame and by the evolution of much white, extremely light powder, the greater part of which settles on the sides of the tube. The bottom of the tube is usually melted out by the heat generated. The white powder was collected and thrown into water. The greater part of it dissolved readily, and this was found by qualitative tests to consist of ammonium and sodium chlorides and of phosphorous compounds. A small portion was found to be insoluble in water.

The results attained in this rough qualitative way seemed to warrant more careful experiment, and accordingly the following apparatus was devised for the work.

A large bell-jar with a diameter of about 26, and a height of about 30 centimeters was fitted to a ground glass plate from which had been cut a portion of sufficient width to admit the glass tube through which pure nitrogen was admitted. The nitrogen, made from molecular equivalent amounts of sodium nitrite and ammonium chloride, was stored in a gasometer, washed through three drying bottles containing strong sulphuric acid and passed over heated copper gauze to remove traces of oxygen and of oxides of nitrogen.

Fitted tightly into the neck of the bell-jar was a wide glass tube which could be raised or lowered at will. In the top of the tube was placed a funnel which served to direct the fall of the materials to be introduced into the small porcelain dish placed within the jar. A slow stream of nitrogen was conducted into the apparatus for a considerable time, the tube in the neck of the bell-jar having been drawn up its full length to facilitate the expulsion of air from the appar-

atus. Without interrupting the flow of gas, small nearly equal portions of powdered sodamide and of phosphorous pentachloride were alternately dropped through the funnel tube which had been partially lowered.

The reaction usually took place at once out, if not, a warmed glass rod inserted through the tube was sufficient to start it.

The energy of the reaction was much diminished by the atmosphere of nitrogen, and if care was exercised to add the materials in very small quantities not much of the white product was projected into the air. There was sufficient heat generated by the union of the first portions to carry the operation on to the end. The time consumed in introducing into the apparatus about 36 grams of phosphorus pentachloride and 30 grams of sodamide was about two hours.

It was noted that the addition of either reagent in excess soon interrupted ignition, but action was at once restored with considerable vigor when change to the other reagent was made.

The apparatus was allowed to cool in the current of nitrogen and upon opening the bell-jar its sides and the bottom plate were found to be covered to a considerable depth with a deposit of exceedingly white, light powder in a state of extremely fine subdivision. In the porcelain dish was a solid core consisting largely of sodium chloride and of traces of the reagents used.

Separation and purification of the sublimate.

To separate the soluble from the insoluble portions was found to be an exceedingly difficult and unsatisfactory task. When the powder was thrown into water much of it went into solution, a small portion settled, but the water assumed and retained a milky appearance which did not disappear after two months standing.

It has been found impossible to separate and purify the residue in this way. If filtration be attempted, the pores of the paper or of the asbestos filter quickly become clogged so effectually that the suction pump is unable to remove the water. The portion of the residue which comes into contact with the filter forms a gummy mass and adheres to it with such tenacity that separation of filter and precipitate

is impossible after drying. The yield of insoluble portion is so small that washing by decantation results in almost complete loss of the precipitate before the soluble portions are removed. Washing with alcohol or other organic solvents is impracticable owing to the quite complete insolubility of the chlorides which it is desired to remove. If the powder is treated with moderately dilute nitric acid an insoluble residue soon settles and the supernatant liquid becomes clear. Specimens of the precipitate for analysis were obtained by treating the white powder twice with a large quantity of dilute nitric acid (one part of acid to four of water), the supernatant liquid being decanted each time as carefully as possible, and once with acid diluted with about twice its volume of water. Each time the beaker containing it was heated to nearly 100° on the water-bath for about 30 minutes. Brown fumes of nitrogen peroxide were evolved on heating and these were ascribed at first to the oxidation of traces of phosphorous compounds which are undoubtedly present. The results of analysis indicate that it is far more likely that the oxidation takes place in the insoluble compound itself.

Acetic acid of 25% strength can also be used to separate the soluble impurities, the powder obtained being somewhat more voluminous. If hydrochloric acid is used there is also rapid settling of insoluble residue, but when this is dried at 100° in an air bath it is semi-liquid and gummy and on further heating to 145° the mass becomes, after cooling, gray, hard, tenacious, and vitreous.

The above acids if diluted further as well as sulphuric acid or solutions of the fixed alkali hydroxides do not effect separation of the two portions. After decantation from the acid washings, the powder was dried in glass vessels at 100° and separated from the glass by the aid of a piece of stiff platinum wire. The yield was about 2.5% of the weight of the white product used.

Purification was also attempted by heating the substance in a combustion tube in a current of dry nitrogen. The escaping gases were permitted to flow through a strong solution of potassium hydroxide. At a dull red heat the compound gave off vapors which condensed in the

cool portion of the tube and also a white vapor which was driven through the potash solution without absorption or change. A gray mass with the taste of sodium chloride and almost entirely insoluble in water was left in the tube. It seemed at the time thus impossible to control purification by this method and the further prosecution of it was abandoned owing largely to the fact that the yield of the compound was so small that the purification by acid was deemed more economical. Properties of the insoluble portion.

The powder thus obtained was a white, nearly tasteless, odorless compound exceedingly inert. Boiling with the strong mineral acids did not affect it and similar treatment with aqua regia or with concentrated potassium hydroxide affected it, if at all, to so slight an extent as to be unnoticable if the action was not prolonged. No solvent could be found for it.

Three methods were devised which were effective in decomposing it.

- 1.- Heated with water in a sealed tube for three hours to 120° , it was decomposed and the solution on opening the tube yielded the odor of ammonia and responded to the molybdate of ammonium test for phosphoric acid.

- 2.- Treated with aqueous solution of hydrofluoric acid and a little sulphuric acid in a platinum crucible, the compound was broken down upon the application of gentle heat. A solution of the residue gave the test for phosphoric acid.

- 3.- Heated to dull redness for four hours in a combustion tube with a mixture of powdered hydroxide and nitrate of potassium, ammonia was evolved and a manganate remained behind. A silver boat was used and a slow stream of dry air was forced over the heated mass.

Analysis.

The above methods were all employed in the analysis of the compound. In the practical application of the first method it was noted that when water alone was used the tube was badly attacked and several grams of silica were separated. It was found best to employ dilute hydrochloric or sulphuric acids for the two-fold purpose of diminishing the separation

of silica and of fixing the ammonia in the non-volatile condition. In all determinations of phosphoric acid by this method, however, it was necessary to separate silica in the usual way before estimating the phosphorus as magnesium pyrophosphate.

The second method was available for the determination of phosphoric acid only. It possessed the advantage of rendering unnecessary the previous removal of silica.

The third method was not free from silica contamination since it was impossible to prevent distillation of the contents of the silver boat or to the combustion tube.

In the first method the ammonium salt was decomposed by distillation with sodium hydroxide, the ammonia being absorbed by a standard acid, while in the third method the ammonia was received directly into the acid.

Table of analyses of the insoluble residue.

Wt. in Gms.	% of P.	% of N.	Method of decomposition.	
0.0664	33.67	19.42	Fusion with KOH & NaNO_3 4 hours.	
0.0739	40.31	20.58	" " " " 5 1/2 hours.	
0.0810	---	21.54	" " " " " " " "	
0.0578	40.31	---	By hydrofluoric acid	
0.0632	40.23	20.75	In sealed tube at 180° .	
0.1108	---	21.50	" " " " " "	
Vitreous mass obtained by hydrochloric acid.				
0.0630	26.63	15.11	In sealed tube at 180° .	
0.1008	27.53	14.57	" " " " " "	
Analysis of portion dissolved out by nitric acid.				
Wt. of material	Wt. of NH_4	Wt. of Cl	Wt. of P	Wt. of Na
3.608	0.2879	1.6998	0.2512	0.7362

Corresponding to:-

	NaCl	1.8735	grams
	NH_4Cl	0.8524	"
	H_3PO_4	0.7944	"
undetermined		0.0777	"
		3.6080	

Interpretation of results.

Whatever the composition of the compound represented by the above analyses may prove to be, it is clear that the phosphorus and the nitrogen stand in the ratio of 1 : 1. The results of the analysis of the compound purified by hydrochloric acid show that it was to a considerable extent broken down and they are therefore not considered.

The analyses correspond to the formula PO_2Nor to some polymer of it. Such formula requires 40.24% phosphorus, 18.22% nitrogen, 41.53% oxygen.

There was found 40.25% phosphorus, 20.55% nitrogen. The excess of nitrogen can well be charged to the fact that in a compound purified by nitric acid, from which the acid could be removed only by washing with weak acid and heating in an air bath to 100° it would be quite impossible to remove all traces of nitrogen derivable from the acid itself.

Schiff 1 has described a compound, POHNOH , made by treating phosphorous pentoxide with ammonia, and this also on decomposition yields phosphoric acid and ammonia. Save for the fact that his compound is soluble in water the description of it corresponds quite exactly with the one here analyzed.

It is certain that the compound formed by the interaction of sodamide and phosphorous pentachloride, whether it be an amide or a nitride of phosphorus, is assuredly not the compound analyzed after the action of nitric acid. The acid undoubtedly oxidizes the compound and may also hydrolyze it. At present, owing to the impossibility of separating the original compound formed from the soluble impurities present, and, owing to other difficulties in the preparation, purification, and analysis of the product which have not been fully detailed, it is largely a matter of theory as to the nature of the most interesting and energetic reaction which sodamide and phosphorous pentachloride present.

In addition to what has been given it may be well to describe at least one attempt at analysis which promised well at the beginning. Without attempting to remove the soluble portions a weighed portion of the freshly formed powder was heated with acid in a closed tube

to 180° with the intention of determining the total phosphorus, nitrogen sodium etc. It was then thought that the proportion of the above elements present in the soluble portion could be separately determined and thus the composition of the insoluble residue arrived at by difference. But experiments showed that in the determination of the ammonia in the soluble portion without removal of the insoluble, the latter was slowly attacked by the boiling sodium hydride. If, as is supposed, the act of washing with nitric acid or with water changes the character of the compound there remain no data from which to calculate analysis results.

Following the enforced abandonment of this process came the unavailing search for other methods of purification of the material for analysis. This part of the work was for the time postponed in the interests of the investigation described on the following pages, but it seems likely that, presuming on the stability of the compound when heated, a method of fractional distillation in a current of pure nitrogen may be devised which will separate the white powder into three portions.

- 1.- An easily volatile mixture of phosphorous and ammonium chlorides.
- 2.- The compound desired.
- 3.- A residue of sodium chloride left behind.

Sodamide and Phosphorus.

Preliminary experiments. —

When sodamide in fine powder and yellow phosphorus in small pieces were heated together under boiling benzene (B.Pt. 79°) there was no action beyond a partial solution of the phosphorus. The experiment was repeated with xylene (B.Pt. 137°) with no evidence of combination having taken place. The same results followed the use of aniline (B.Pt. 183°) although the aniline was attacked by the reagents with the formation of complex organic products. Finally heavy lubricating (paraffin) oil was employed (B.Pt. 214° or more) with no better results. But when the two substances were brought together in a test tube combination took place with great energy on slight warming of the tube. An incrustation of red phosphorus was formed on the tube, the bottom of which was usually melted out in the reaction. Particles of an almost black substance, formed by the reaction, produced, when thrown into water, a spontaneously inflammable gas and emitted a most pronounced disagreeable odor. Red phosphorus and sodamide heated together rather more strongly produced a similar compound.

Preparation of the material.

Attempts were then made to prepare the compound in test tubes, flasks etc. properly supplied with a stream of pure, dry nitrogen by feeding into the apparatus alternately small amounts of phosphorus and of sodamide. However the heat evolved by the reaction always shattered the glass and prevented the preparation of any considerable amount.

Porcelain vessels could be used without fear of breakage, and the experiment whereby about 12 grams could be prepared at once was carried out as follows.

The bottom of a wide mouthed bottle of about three liters capacity was covered with glass beads to a sufficient depth to hold in place a large porcelain crucible about 30 X 30 millimeters. The bottom of the crucible was kept from direct contact with the bottom of the bottle that the latter might not be cracked by local heating.

Through the neck of the bottle was passed a gas delivery tube of small bore reaching to the bottom of the bottle and also a wide glass tube

about 30 ~~mm~~ millimeters in diameter which could be raised at the beginning of the experiment to assist in driving out the air, but lowered almost to the mouth of the crucible when the reagents are to be dropped in. A second gas delivery tube was passed into this wide tube and connected by a Y with the same nitrogen apparatus described in the reaction with sodamide and phosphorous pentachloride. By means of stopcocks nitrogen could be delivered into the bottom of the bottle, into the vicinity of the reacting substances, or simultaneously through both tubes at will. The stream of nitrogen was not discontinued at the end of the experiment until the apparatus was quite cool. The reaction proceeded with far less vigor in nitrogen than in air. The heat of a warmed glass rod was sufficient to start the reaction, which then proceeded by its own heat as long as materials were added to the crucible. Precautions had to be employed to prevent too great rise in temperature, for with such rise much of the phosphorus was converted into the red modification. It has not been found possible to prevent entirely this formation of red phosphorus, but under favorable circumstances not much in excess of 1% of the compound consists of this element.

When the air had been displaced, the finely powdered sodamide and the phosphorus in small pieces were dropped through the long tube into the crucible in small successive portions. The phosphorus was dried as thoroughly as possible by absorption under or, better, by benzene. It was found advisable to have the phosphorus in slight excess since such excess could be removed by heating with carbon disulphide; no solvent for excess of sodamide could be found which did not also break down the compound formed by the reaction. The attempt was made to remove the excess of sodamide in the first portion made, by washing with absolute alcohol, for it is known that alcohol acts upon sodamide in the sense of the following equation:-



but it was found that the entire compound was decomposed with evolution of phosphine. In fact even the treatment with carbon disulphide was observed to set free appreciable amounts of ammonia and of phosphine and this was taken as a significant indication of the instability

of certain components of the reaction.

If the material was removed from the atmosphere of nitrogen before cooling it took fire spontaneously, or if it was subjected to any friction in the dry state before removal of the excess of phosphorus the same result happened. The crucible was therefore allowed to cool completely and its contents were then moistened with carbon bisulphide which had been purified by redistillation and allowed to stand over calcium chloride to remove the last traces of water.

While thus moistened the hard almost black substance was broken loose from the crucible, transferred to a mortar, ground to a powder under carbon bisulphide and then transferred to a small flask. The latter was provided with a return condenser. In this flask the material was heated to the boiling point of the carbon bisulphide by means of a hot water bath, the solvent removed by decantation and a fresh portion added. The powder was then dried at the ordinary temperature in long tubes through which a current of dry nitrogen was conducted.

When dry it was transferred to glass-stoppered weighing bottles and kept in a phosphorus pentoxide desiccator.

Properties.

As thus prepared the material is chocolate red in color. It is exceedingly sensitive to even traces of moisture and gives off continually a most disagreeable odor suggestive of garlic. Exposed to the air for a short time it deliquesces and becomes somewhat lighter in color. Heated in the air it gives off quantities of ammonia and of phosphine and the sodium salt of hypophosphorous (and probably also of phosphorous) acid is left behind. Heated in a stream of dry carbon dioxide it gives off the same two gases and there remains sodium carbonate, ^{hho} hypophosphite and phosphine. Water, dilute acids and alcohol break it down in the same way but if alcohol is used the phosphine is not inflammable. Hydrogen is also evolved in considerable quantity by decomposition in the wet way. Absolute ether, chloroform or benzene are without apparent action on the compound.

Historical.

Before taking up the analysis of this material it is thought best to

refer in a brief manner to the work which has been done along similar lines in so far as it may have any bearing upon this work.

Gay Lussac and Thénard and also Davy supposed that phosphides of the alkali metals could be formed by heating the elements together in nitrogen.

In 1828, Magnus¹ devised a method for the preparation of potassium phosphide, K_3P , which was later used by Vigier² in preparing the similar sodium phosphide. Phosphorus was melted under petroleum (B.Pt. 120°) and bits of potassium were added from time to time. The excess of oil was distilled off, the compound boiled with carbon bisulphide and dried at low temperature in a current of dry carbon dioxide. He stated that the compound separated carbon as well as phosphine when treated with water or dilute acids, and that although he rectified the petroleum several times and took great precautions to employ carbon-free potassium and phosphorus he was not able to get the phosphide in a state of purity. Vigier's sodium phosphide was described as a black compound. In the course of this work his experiments were repeated resulting in a verification of his method and description and, in addition, a partial analysis was made which will be referred to in its proper place. Vigier used his phosphide in an organic research and he made no attempt to purify or to analyze it.

Magnus gives nothing but the formula for his potassium phosphide, making no statement as to any analyses upon which he based his conclusions.

Rose³ caused potassium and phosphorus to combine in a flask in the presence of hydrogen. At the end of the experiment the excess of phosphorus was distilled off. He obtained a crystalline mass of the color of "laminated copper".

Bunsen⁴ showed that sodium phosphide was formed by heating sodium and

1. *Ann. Chem. Phys.* 17, 527.

2. *Chem. News* 1861, 273.

3. *Ann. Chem. Phys.* 12, 247.

4. *Ann. Chem. Pharm. Liebig* 183, 292.

sodium phosphide together in a tube and he recommended this as a qualitative test for the presence of phosphorus.

The phosphides of calcium, tin, zinc, copper, magnesium, iron, and aluminum have been made ¹ and their composition and properties established. The phosphides of the heavy metals, as would be supposed, are much more stable than those of the alkalis.

Sodammonium, NaNH_2 , and potassium, KPH_2 , have in the hands of Hugot and Joannis, working independently, been of considerable importance. These two reagents are made by the action of liquid ammonia on sodium or on potassium. They decompose slowly at ordinary temperatures ² and a little more rapidly in the light than in the dark, forming sodamide or potassamide and hydrogen. Sodammonium in excess, red phosphorus and sodium left in contact for several days formed $\text{P}_2\text{H}_2\text{Nag}$, (NagP.PH_2) , sodamide and ammonia. The phosphide is described as a yellow crystalline body, yielding phosphine in the presence of moisture ³. The authors claim that if the red phosphorus is in excess $\text{P}_2\text{H}_2\text{KPH}_2$ is formed which loses its ammonia at 180° . It is always more or less contaminated with potassamide. With sodium $\text{P}_2\text{H}_2\text{Na.PH}_2$ is formed which becomes P_2H_2 at 180° . If no sodium or potassium is used or if phosphine be led into sodammonium or potassammonium the substituted phosphines NaNH_2 and KPH_2 are formed ⁵.

The chemistry of the phosphides of hydrogen is also closely interwoven with this work because the phosphine produced in the decomposition of the compound by water was relied upon as a measure of the amount of sodium phosphide in it.

It was Thénard ⁶ and, later, Guttierari ⁷ who first separated and

1. Centralblatt 1890, 2, 642.

Bull. Soc. Chim. (5), 27, 558.

2. Compt. Rend. 112, 392.

3. Ibid. 123, 1719; 2 127, 553.

4. Ibid. 121, 206.

5. Ibid. 119, 557.

6. Ann. Chem. Pharm. Liebig 55, 27.

7. Ber. d. Chem. Ges. 25, 1174.

determined the constitution and properties of gaseous, liquid and solid phosphines. The former also noted the presence of hydrogen as a free constituent in the ordinary phosphine.

Hoffman¹ showed that in all the common methods of producing phosphine the gas was diluted with from 3% to 80% of hydrogen (volumetric). When phosphine was made in the ordinary way by heating an aqueous solution of potassium hydroxide with yellow phosphorus only from 10% to 40% of the gas obtained was phosphine. Alcoholic potash gave about 45% phosphine under similar circumstances.

If calcium phosphide was used the yield of phosphine was better but^{the phosphine} was far from pure. The amount of hydrogen was very changeable and was not accounted for. Even the decomposition by heat of pure phosphoric acid yielded a phosphine which contained at least 3% of hydrogen. The decomposition of pure phosphonium iodide, PH_4I is the only method of obtaining pure phosphine. He also pointed out that fuming nitric acid as well as the vapor of chlorine and of bromine render non-inflammable phosphine self-inflammable.

Boaroux² pointed out that temperature has something to do with the amount of hydrogen produced: in the case, at least of the decomposition of certain phosphides. When aluminum or magnesium phosphide are decomposed with water they yield phosphine slowly. If the water be above 50° or if acids are used much hydrogen is developed; if ice-water is used no hydrogen is formed.

Analysis.

The methods of analysis employed were volumetric gas determinations with the apparatus described for the examination of sodamide, and special quantitative determinations in the gravimetric way.

Volumetric:-

A freshly prepared solution of cuprous chloride in concentrated hydrochloric acid was placed into a Bunsen gas pipette and made use of to absorb the phosphine. The hydrogen was determined by explosion in

1. Ber.d.Chem. Ges. 4,200.

2. Bull.Soc. Chim. (3),27,568.

a eudiometer over mercury with electrolytic oxygen. The ammonia was not measured volumetrically but was absorbed along with the carbon dioxide with which the apparatus was filled at the beginning of the experiment by a moderately strong solution of caustic soda in a Hempel's burette. The process of analysis was as follows:--

After the apparatus (see Fig's. 23-3) had been filled as previously described with dry carbon dioxide, the material was weighed in and carbon dioxide was again conducted through until the air was entirely displaced. The Hempel burette capillary, completely filled with liquid, was attached. Diminished pressure was produced by lowering the communicating arm of the burette and, by cautious control of the stopcock of the funnel, water was slowly admitted dropwise, allowing a considerable interval between drops for the absorption of the carbon dioxide and ammonia and for partial cooling of the generator.

The decomposition was very violent but in the atmosphere of carbon dioxide the phosphine did not ignite. In about ten minutes after the beginning of the experiment the reaction was complete and water could be admitted rapidly to drive over all of the gases into the burette. The solution remaining in the generator was strongly alkaline, responded to the tests for hypophosphorous acid and contained a small residue of red phosphorus. The burette was then disconnected and well shaken to complete the absorption of carbon dioxide and ammonia and after the lapse of ten minutes the volume of the gas was noted. The burette was then connected with the Bunsen pipette containing the acid cuprous chloride and the gas forced over into it. Phosphine forms colorless needles of cuproso-dichlorophosphonium dichloride, $\text{Cu}_2\text{Cl}_2 \cdot 2\text{PH}_3$ ¹.

After shaking five minutes the remaining gas was returned to the burette and read as before after ten minutes. The difference was calculated as per cent of phosphine to total, non-absorbed gas.

Measured portions of the remaining gas were then passed into the eudiometer, exploded with oxygen, and the amount and purity of the

hydrogen determined by the ordinary eudiometric methods.

Owing to the continuous decomposition which the material undergoes, it was not deemed wise to make large quantities of it at one time, nor was it possible with the apparatus employed. The analyses developed the fact, which was to be expected, that the composition of the three portions of material made at different times was not identical, as well as the fact that analyses made after considerable intervals showed that the material underwent constant slow deterioration. In other words it was a chargeable mixture whose nature prevented the possibility of isolation of the desirable components in pure condition.

Analyses (volumetric) of the three portions made are here given in tabular form. Regarding the general method of preparation it can be said that the first portion was known to contain some excess of unchanged sodamide. The sodamide used in its preparation was that called "sodamide I" of which the analyses already given show that it yielded considerable nitrogen and hydrogen on decomposition with water. The remaining portions were made with sodamide III, (which yielded very little gas by treatment with water) and with phosphorus in large excess. Precautions were taken to insure the complete combination of the two reagents. In the preparation of portions II & III slight changes only were made in details of temperature, methods of bringing the reagents together, washing etc.

Where blanks occur no determination was made, but sufficient explosions of the gas derived from portions two and three were made to show positively that no body yielding free nitrogen was present either in the freshly made material or formed in it or standing. The nitrogen in portion I is due solely to the excess of sodamide as pointed out.

Table of volumetric gas analyses of the product of the phosphorus
sodamide reaction.

Portion I. Excess of sodamide I.					
Wt in gms.	Total gases in C.C. not absorbed by NaOH	% PH ₃	% H ₂	% N ₂	Remarks.
0.8664	26.75	57.01	45.77	7.22	
0.1071	21.05	52.49	38.66	9.13	
0.9243	22.45	52.53	---	---	
0.6834	19.43	49.71	44.69	5.60	
0.5390	11.25	47.71	---	---	
0.9612	31.15	47.35	49.85	6.80	
1.1212	34.45	47.17	49.74	6.09	
0.4446	15.05	46.84	---	---	
0.7050	24.40	43.72	---	---	
1.1614	35.95	43.37	48.04	7.09	
0.6109	19.55	43.80	44.44	5.73	
1.9513	35.45	45.75	---	---	
0.7637	23.15	45.01	---	---	
Portion II. Sodamide III. Phosphorus in excess. Simultaneous addition of					
0.3043	69.05	26.13	71.84	0.30	reagents. Temp. kept low by ice.
0.8095	37.95	24.65	75.55	---	
0.7800	32.35	24.13	75.87	0.00	
0.3734	59.95	19.93	80.07	0.00	
0.3742	73.25	19.74	80.26	---	
0.3752	31.30	18.99	81.01	---	
Portion III. Sodamide III. Phosphorus in excess. Successive addition of					
0.4123	57.	13.14	85.35	---	reagents. No ice.
0.4190	33.80	15.04	84.93	0.00	
0.3069	57.35	14.65	85.05	0.00	
0.4735	37.30	14.85	85.15	---	

These analyses, made during the course of several weeks, were purposely varied in minor details in order to determine whether any appreciable change in the amount and nature of the gases occurred.

Thus at times dilute acids were used in place of water to decompose the material; the determination of hydrogen was made both by explosion over water at nearly normal pressure and over mercury at diminished pressure etc. It could not be shown that these or other details affected the analysis figures. The observation of Hoffner¹ that the ratio of phosphine to hydrogen is very variable was confirmed, but it seems to be largely due to the fact that the phosphide is not homogeneous and even if it could be rendered so by trituration, its instability in air would soon destroy any homogeneity.

Although Bodroux¹ had shown temperature to be a controlling factor in the amount of hydrogen obtained in the case of aluminum and magnesium phosphides, it was found in similar experiments with the sodium phosphide made after the method of Vigier that only a slight change could be detected.

0.2987 grams decomposed by water at 20°C yielded 38.01% PH_3 (volum.)

0.3467 " " " " " 0°C, generator in a bath of ice water yielded 40.42% phosphine.

The hydrogen is, of course, the difference between these figures and 100% and it will be remembered that Bodroux obtained no hydrogen with the use of ice water.

The difference in amount of phosphine obtained from the first portion as compared with the other two is striking and, at the same time, it will be noted that the proportion of gases not absorbable in sodium hydroxide is more than twice as great in the last two portions as in the first.

Alkalinity could not be determined in the decomposition of the material by dilute acids or water. Attempts were made to thus determine it by causing the generated gases to bubble through sulphuric acid of six-normal strength contained in a Pelicot's tube.

1. Loc. Cit.

The rush of gas was, however, so rapid at first, even with the greatest care to add water slowly, that ammonia to an appreciable extent was carried through into the Hempel's burette. A weighed portion of the material was then placed in a small weighing bottle and lowered into a pressure bottle containing some six-normal hydrochloric acid. The top was immediately adjusted and the apparatus was set away 24 hours for the vapor of the acid to slowly attack the material. At the end of that time acid and substance could be brought into intimate contact by tilting the bottle without development of dangerous pressure. The ammonia salt and excess of acid were then washed into a flask, and the ammonia was determined by the aid of a standard acid in the usual way. 0.2416 grams of material gave 22.49% ammonia.

In a second experiment the following apparatus was employed. A small flask containing concentrated hydrochloric acid was connected with a gas washing bottle filled with the same acid. The exit from this bottle led into three U-tubes, the first contained the weighed substance, the other two contained dilute sulphuric acid. The apparatus was connected by an empty flask to the suction pump. By gentle heating of the first flask under diminished pressure, gaseous hydrochloric acid could be driven through the apparatus over the compound and all its ammonia in the course of 1 1/2 hours. Continuation of the experiment was fixed as chloride or sulphate of ammonia. Dilute acid was finally brought into contact with the material and the contents of the three tubes were distilled from excess of alkali into standard acid as above. 0.4484 gram of material gave 22.80% ammonia.

The method has the advantage of rapidity but is more complicated. Gravimetric determinations.

Sodium was determined gravimetrically as sulphate. The phosphorus was removed by oxidation with nitric acid, precipitation by lead acetate and lead carbonate, and, after filtration from the phosphates, excess of lead was removed by hydrogen sulphide.

0.4627 grams of material gave 0.6518 grams of Na_2SO_4 , equal to 44.22% Na.
 0.1558 " " " " 0.2038 " " " " 43.63% Na.

Determinations of phosphorus.

In the determination of phosphorus the pressure bottle method was employed. At first the attempt was made, after introducing the small tube containing the material into the bottle in which was some dilute nitric acid, forcing the substance immediately into solution.

For this purpose a long pair of tongs was used to grasp and tilt the bottle. But such sudden pressure was developed that the bottle was broken into small pieces by the force of the explosion.

In subsequent experiments the small cups of material were allowed to stand in an upright position within the bottle for a long time.

Fuming nitric acid was placed in the bottle because it was certain that its vapors would more speedily oxidize volatile phosphorus compounds and complete the oxidation to phosphoric acid of lower oxygen compounds of phosphorus. The action within the pressure bottle was usually violent. In from one to two hours after closing the bottle an explosion with flame usually occurred within of sufficient force to shatter the weighing flask which contained the substance.

But, owing to the fact that small weights of material were used, that the pressure bottle had a capacity of 500 cubic centimeters, and that in the first one or two hours most of the ammonia had been "fixed", the bottle withstood the force of the shock.

After the lapse of several hours the pressure bottle was merely heated in a water-bath without removal of the stopper; this was done to make sure of the oxidation of any phosphine during the process.

The bottle was then opened and its contents were evaporated on the water-bath almost to dryness. The phosphorus was determined as manganous hypophosphite. The determination was verified by first precipitating a second portion to be analyzed with arsenious sulfide and then with a special mixture.

In a third determination, to show that there was no conversion of the phosphates into meta-phosphates, the solution was boiled with a large excess of water for thirty hours, the water lost at evaporation being restored from time to time. For results in all these methods agreed well within the limits of experimental error.

0.2496	grams of material	0.1476	grams of anal. hypophos. at 12.46°P
0.1637	" " " "	0.0986	" " " " 16.45°P
0.1750	" " " "	0.1084	" " " " 16.91°P

Reactions and Composition.

1.- Alluding to the products of the reaction between selenium and phosphorus the term "material" has been deliberately used. The reasons for this, some of which have been given, may be summarized thus:-

- 1.- It has been shown by analytical results that successive preparations do not possess the same composition.
- 2.- The products of its decomposition in water or acids are numerous.

Phosphine, phosphine, ammonia, sodium hypophosphite, sodium hydroxide, and red phosphorus have been discovered in the decomposition residue and there is no reason to believe that salts of these acids and of phosphoric acid are also formed. There is no one salt of definite composition which can be supposed to be formed by these two reagents. viz. sodium and selenium phosphorus, capable of including all these products simultaneously in the molecule as formed.

3.- It has been shown that the insolubility of the compound in the presence of alkalis, acids, and organic solvents is exceptional. While, on the other hand, the compound dissolves in water, alcohol, ether, and dry dipropyl ether upon an analysis of its constituents. Owing to these facts the attempt to purify the compound or to isolate any of its constituents has not been successful.

4.- Selenium does break down in the presence of substances capable of driving down its valence to +2 or +3. Thus, in the union with water, the loss of sulphur in the solution is the least the selenium and the sulphur group. On the other hand, it has been shown that sodium amide reacts with many organic compounds especially the organic oxides one of the acidic hydrogen atoms in selenium is substituted by the organic residue.

5.- The behavior of phosphorus is even more anomalous. The list of phosphorous compounds prepared by chemists from the reaction of

Marius and Rose to the present, and finally to the distribution of the principles of philosophy and the sciences, and the high degree of criticism, based on the scientific and philosophical.

1. A. a. $2\text{P} + 3\text{H}_2\text{O} \rightarrow \text{P}_2\text{O}_3 + 3\text{H}_2$
 a.) $2\text{P} + 3\text{H}_2\text{O} \rightarrow \text{P}_2\text{O}_3 + 3\text{H}_2$
 b.) $2\text{P} + 3\text{H}_2\text{O} \rightarrow \text{P}_2\text{O}_5 + 3\text{H}_2$
 2. Assuming it to react with phosphoric acid, then the acid would,
 a.) $\text{P} + 3\text{H}_3\text{PO}_4 \rightarrow \text{H}_3\text{PO}_3 + 3\text{H}_2$
 a.) $\text{P} + 3\text{H}_3\text{PO}_4 \rightarrow \text{H}_3\text{PO}_3 + 3\text{H}_2$

- [illegible]

under the influence of the action of the solvent, the reaction which was observed. After the reaction had ended, the neutral solution, or, at least, (which could not be seen) the reaction mixture, passed through the filter and the precipitate was washed.

After the reaction had ended, the solution was washed. The solution was then there was a solution of 7.56 g. of water at 10. The solution was then filtered and the filtrate was washed. The solution was then filtered and the filtrate was washed. The solution was then filtered and the filtrate was washed.

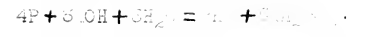
The solution was then filtered and the filtrate was washed. The solution was then filtered and the filtrate was washed. The solution was then filtered and the filtrate was washed. The solution was then filtered and the filtrate was washed.

Secondly, the solution was then filtered and the filtrate was washed. The solution was then filtered and the filtrate was washed. The solution was then filtered and the filtrate was washed. The solution was then filtered and the filtrate was washed.

Thirdly, the solution was then filtered and the filtrate was washed. The solution was then filtered and the filtrate was washed. The solution was then filtered and the filtrate was washed. The solution was then filtered and the filtrate was washed.

The final solution was then filtered and the filtrate was washed. The solution was then filtered and the filtrate was washed. The solution was then filtered and the filtrate was washed. The solution was then filtered and the filtrate was washed.

For the purpose of the experiment, the solution was then filtered and the filtrate was washed. The solution was then filtered and the filtrate was washed. The solution was then filtered and the filtrate was washed. The solution was then filtered and the filtrate was washed.



Without doubt the reaction is far more complicated than for the sake of clearness we, be assured to take place in the following reactions:

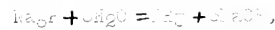
- a.) $4F + 8.5H = 2HF + 4F(H)g$
- b.) $2.5F + 7H_2O = 5H_2 + 4HF + 3.5O_2 + 4H$
- c.) With the case of a salt as to follow the case,
 $2F(H)g + 4H = 2Fg + 2H_2O + 4H_2$

whence by combination of above three and reduction to simplest terms there result the correct reaction:-



That d.) more nearly expresses the correct reaction is supported by the fact that both of the above reactions can be made to be correct in the solution, when the reaction mixture was heated and stirred by the application of the law of conservation of energy described. It is not claimed that this as written represents the exact composition of the products, it shows merely that as the reaction proceeds at least two of the acids or vapors are either evolved or are generated in the usual way.

In a similar way we might have also written the above as $4Fg + 5H_2O$ units in which case:-



but in this case also such a reaction is not complete thermodynamically representing:-



and to account for the evolution of the sodium salt of trihydrofluoroboric acid:-



References should be made to the above of the analysis of the product in the laboratory. Analysis gives 22.64. 1H₂ equivalent, and 1.0 1H₂. That this is not present as sodium fluoride is well known from 1. The appearance of the product of the reaction is a white solid, 2. its uniform dark brown color, 3. its uniform distribution of the inter-molecular bonds. In no case, 4. is it soluble, 5. is it not visible.

